



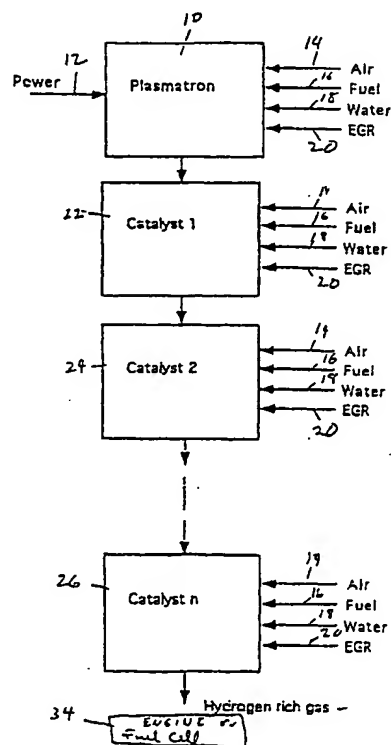
## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(21) International Application Number: <b>PCT/US99/25179</b> (22) International Filing Date: <b>27 October 1999 (27.10.99)</b> (30) Priority Data: 09/182,537                      29 October 1998 (29.10.98)                      US (71) Applicant: <b>MASSACHUSETTS INSTITUTE OF TECHNOLOGY [US/US]; 77 Massachusetts Avenue, Cambridge, MA 02142 (US).</b> (72) Inventors: <b>BROMBERG, Leslie; 176 Wilshire Drive, Sharon, MA 02067 (US). RABINOVIC, Alexander; 404 Paradise Road #3L, Swampscott, MA 01907 (US). ALEXEEN, Nikolai; Pavla, Korchagina Street 15-00, Moscow, 129278 (RU). COHN, Daniel, R.; 26 Walnut Hill Road, Chestnut Hill, MA 02167 (US).</b> (74) Agent: <b>PASTERNAK, Sam; Choate, Hall &amp; Stewart, Exchange Place, 53 State Street, Boston, MA 02109 (US).</b>	(81) Designated States: <b>CA, JP, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</b>  <b>Published</b> <i>With international search report.</i>	

(54) Title: **PLASMATRON-CATALYST SYSTEM**

## (57) Abstract

The system generates hydrogen-rich gas and comprises a plasmatron (10) and at least one catalyst (22) for receiving an output from the plasmatron (10) to produce hydrogen-rich gas. In a preferred embodiment, the plasmatron (10) receives as an input air (14), fuel (16) and water/steam (18) for use in the reforming process. The system increases the hydrogen yield and decreases the amount of carbon monoxide.



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## PLASMATRON-CATALYST SYSTEM

This application is a continuation-in-part of U.S. Application Serial No. 08/589,119 filed January 19, 1996 for Rapid Response Plasma Fuel Converter Systems.

### Background of the Invention

This invention relates to a plasmatron-catalyst system which can maximize hydrogen yield and decrease the amount of carbon monoxide.

The pending U.S. Application mentioned above, of which this application is a continuation-in-part, discloses and claims the use of a rapid response plasmatron for converting hydrocarbon fuels into hydrogen-rich gases. This process may be carried on-board vehicles.

Converting hydrocarbon fuels into hydrogen-rich gas (reforming) can be achieved with a plasmatron reactor. There are many advantages of using a plasmatron in the reforming process. Advantages include fast response (less than one second), adequate conversion into hydrogen-rich fuel, compactness (high hydrogen productivity), robustness (stable process), and the ability of the plasmatron to use many fuels, including hard-to-reform gasoline, diesel and biofuels.

For internal combustion applications, the hydrogen purity is not of great importance. High conversion efficiency into hydrogen is not necessary, since the low weight hydrocarbons that accompany the hydrogen produced by the plasmatron are also good fuels for use in internal combustion engines. More important is to minimize the energy consumed in the plasmatron during the reforming process.

U.S. Patent Nos. 5,425,332 and 5,437,250 disclose plasmatron-internal combustion engine systems and the teachings of these two patents are incorporated herein by reference. Plasmatrons of the type used in the present invention are described in detail in these two patents.

In the previous application mentioned above, partial oxidation is the preferred method of reforming. An advantage of partial oxidation is that it eliminates the need for storing additional liquids on-board vehicles. Also, in that application, a fraction of the fuel is reformed in order to allow the introduction into the cylinder of an engine hydrogen-rich gas to improve the combustion process. Since the intention in that application was not to reform all of the fuel, the issues of efficiency, although still relevant, do not drive the design of the plasmatron system.

The previous application discloses the use of plasma catalysis on-board vehicles. The process of converting the hydrocarbon into hydrogen rich gases by the use of plasma catalysis addresses mainly the energy requirement in the plasmatron in the reformation process. Plasma catalysis, as used for applications in internal combustion engines, can decrease the electrical energy requirement. The earlier patent application did not suggest the use of catalysts to maximize hydrogen yield nor to decrease the amount of CO (carbon monoxide) that is produced in the partial oxidation process (The hydrogen yield is defined as the ratio of the hydrogen in the reformat to the amount of hydrogen content in the fuel).

The earlier pending application did not extend plasma catalysis into the context of fuel cell vehicles and stationary fuel cells in which very high hydrogen yields and low energy consumption are required.

The requirements on a reformat for fuel cell applications are very different from those for use of hydrogen rich gas in internal combustion engines. As described above, for application to internal combustion engines, it is not necessary to have high yields, a very efficient process or very clean gas. As used herein, clean gas is defined to be gas with small concentrations of CO, since CO is a poison to some types of fuel cells that are presently being considered for both stationary and vehicular applications, of which the PEM fuel cell is the most advanced candidate. U.S. Patent No. 5,409,784 discloses plasmatron/fuel cell combinations and the teachings of this patent are incorporated herein by reference.

The pending patent application of which this application is a continuation-in-part also did not disclose the possible use of water/steam in the reforming process.

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### Summary of the Invention

10 In one aspect, the plasmatron-catalyst system of the invention for generating hydrogen rich gas includes a plasmatron and at least one catalyst for receiving an output from the plasmatron to produce hydrogen rich gas. In a preferred embodiment, the plasmatron receives as an input air, fuel and water/steam. The plasmatron may also receive exhaust gas from an engine or fuel cell. It is preferred that the at least one catalyst receive as an input air, fuel and water/steam. The catalyst may also receive exhaust gas from an engine or fuel cell.

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In another embodiment, the at least one catalyst includes a heat exchanger in heat exchange relation with the catalyst to preheat the air, fuel and water/steam. One embodiment includes a plurality of catalyst sections wherein each catalyst section receives additional air, fuel or water/steam.

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In another aspect, the plasmatron catalyst system further includes a fuel cell for receiving the hydrogen rich gas, the hydrogen rich gas having reduced CO content. The fuel cell may be in a vehicle or in a stationary setting.

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In another embodiment, the plasmatron is followed by fuel injection system for a partial oxidation process, the fuel injection system followed by a catalyst for improved yields, the catalyst followed by water/steam injection and a water-shift reformer catalyst whereby hydrogen concentration is increased and CO concentration is decreased. In any of these embodiments, the catalyst may be a water-shifting catalyst. The catalyst may also be a partial oxidation catalyst or a steam reforming catalyst. In yet another embodiment, the catalysts are a combination of partial oxidation, steam reforming or water-shift catalyst with possible addition of water/steam in between adjacent catalytic regions.

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In another embodiment, the steam reforming catalyst is followed by a water-shifting catalyst, with or without additional water/steam injection prior to the water-shifting catalyst.

5           The present system may be operated in a less efficient non-catalytic mode of operation during cold start followed thereafter by more efficient catalytic plasma reforming after the catalyst reaches operating temperature. The water/steam may be obtained from oxidation of hydrogen in a fuel cell or by combustion in an engine such as a diesel engine. The water-steam may also be obtained from the exhaust of a diesel  
10           engine.

          In yet another aspect, the hydrogen rich gas is delivered to a catalytic converter of an internal combustion engine wherein the enthalpy of the hydrogen-rich gas preheats and/or activates the catalyst in the catalytic converter. The hydrogen-  
15           rich gas produced by the system of the invention may also be used for reducing processes in metallurgy and chemistry. The hydrogen-rich gases may also be used for hydrogenation as in food processing and fuel upgrading.

          In yet another embodiment, the CO content of the reformat is decreased by  
20           the use of a non-thermal, catalytic reaction to selectively oxidize the CO to CO<sub>2</sub>.

#### Brief Description of the Drawing

          Fig 1. is a block diagram of an embodiment of the invention illustrating  
25           multiple catalyst sections.

          Fig 2. is a block diagram of an embodiment of the invention including a heat exchanger.

          Fig 3. is a block diagram of an yet another embodiment of the invention.

          Fig 4. is a block diagram of an embodiment of the invention including a  
30           catalytic converter.

          Fig 5. is a block diagram of an embodiment of the invention including a non-thermal plasma catalyst.

Description of the Preferred Embodiment

Water/steam can be used to achieve several objectives in the reforming process. These objectives include use in a water-shift reaction, downstream from the plasmatron and reactor, in order to reduce the CO concentration and increase the hydrogen concentration. Water/steam can also be used to perform steam reforming in which the water/steam reacts with the hydrocarbon fuel to produce hydrogen and CO. Water/steam can also be used in an autothermal reaction in which both air and water/steam are used in order to insure that the exothermicity of the partial oxidation process is balanced by the endothermicity of the steam reforming reaction. In this case, the reforming reaction is energy neutral. The use of water/steam, oxygen and fuel in a plasmatron reactor forms a continuum of possibilities. In the case of partial oxidation, the maximum hydrogen yield is 100%, while when water/steam is added the hydrogen yield can be larger than 100% by virtue of the release of hydrogen from the water/steam.

It will be appreciated by those skilled in the art that exhaust gases, either from a fuel cell or an internal combustion engine may be used as an input to the plasmatron for reforming. In this case, the reformed gas composition is nitrogen, CO, CO<sub>2</sub>, and water.

It has been demonstrated experimentally by the inventors herein, that by using catalysts downstream from the plasmatron, the electrical energy consumption in the plasmatron is reduced substantially (by a factor of 9) with increased hydrogen yields (approaching 100%) and with relatively small CO concentrations (at the present time, about 1-2%, but possibly smaller in the future with improved reactor design).

The need to preheat the catalyst slows down the response of a system operating in plasma catalysis mode. Fast response is needed, especially for on-board applications, for the fast generation of hydrogen during initial operation of a vehicle after a prolonged shut down. In order to allow for rapid response, the mode of operation of the plasmatron is varied. During cold starts, the plasmatron operates

with larger electrical input, resulting in gases with high enthalpy, that allows for high yields without the need of the catalyst, but at the expense of increased energy consumption. In other words, during cold start the system operates in a non-catalytic mode. Once the catalysts are warmed up, the plasmatron energy input is decreased to the steady state level allowed by the more efficient plasma catalyst.

The hydrogen rich gas from the plasmatron may also be introduced into the catalytic convertor that is used to control emissions from an internal combustion engine. The hydrogen and radicals produced by the plasmatron interact with the catalyst, making it more active. In addition, combustion of the hydrogen rich gas on the catalytic surface increases the temperature of the catalyst, and can be used for quick turn-on of catalyst during cold start-up. The long-lived radicals produced by the plasmatron also enhance the catalytic performance of the convertor.

The hydrogen productivity in plasma-catalytic mode, with water/steam injection, can be very high, generating about 10 cubic meters of hydrogen per liter of reactor.

With reference now to Fig. 1, a plasmatron 10 is supplied with electrical power 12. It is contemplated that this plasmatron will also receive as input air 14, fuel 16, water 18 and optionally exhaust gas 20. In this embodiment, the output of the plasmatron 10 passes into a first catalyst section 22 and from there into a second catalyst section 24. Any number of additional catalyst sections may be added up to catalyst  $n$  illustrated at 26 in Fig. 1. The catalyst used in the catalyst sections may be a water-shifting catalyst, a partial oxidation catalyst or a steam reforming catalyst.

With reference to Fig. 2 a, a heat exchanger 28 is provided in heat exchange relation with catalyst  $n$ . The heat exchanger 28 will preheat the air, fuel and water before it enters the plasmatron 10. A similar arrangement is shown in Fig. 3 in which the heat exchanger 28 serves to preheat fuel, air and water before it enters the catalyst 22.

A very important aspect of the present invention is illustrated in Fig. 4. In this embodiment, the output of the plasma and the multiple catalyst stages is directed to a catalytic converter 30 such as conventionally used with internal combustion engines. In this case, the hydrogen-rich gas and radicals produced by the plasmatron interact with the catalyst making it more active. In addition, air and fuel may be injected into the catalytic converter 30 so that combustion of the hydrogen-rich gas on the catalytic surface increases the temperature of the catalyst and can be used for quick turn-on of the catalyst during cold start up.

Finally, with reference to Fig. 5, the output of the plasmatron-catalyst system is introduced into a non-thermal plasma catalyst of 32 which produces a hydrogen-rich gas with a low CO content.

With reference again to Fig. 1, those skilled in the art will recognize that hydrogen rich gas from the last catalyst stage may be delivered to an engine or fuel cell 34.

It is thus seen that the present invention results in a rapid response plasmatron/catalyst system which can maximize the hydrogen yield and decrease the amount of carbon monoxide by using water/steam in the reforming process.

It is recognized that modifications and variations of the present invention will occur to those skilled in the art and it is intended that all such modifications and variations be included within the scope of the pended claims.

What is claimed is:

- 1        1.        Plasmatron-catalyst system for generating hydrogen-rich gas comprising:  
2                a plasmatron; and  
3                at least one catalyst for receiving an output from the plasmatron to produce  
4                hydrogen-rich gas.
- 5        2.        The system of claim 1 wherein the plasmatron receives as an input air, fuel  
6                and water/steam.
- 7        3.        The system of claim 2 further including the plasmatron receiving exhaust gas  
8                from an engine or fuel cell.
- 9        4.        The system of claim 1 wherein the at least one catalyst receives as an input air,  
10               fuel and water/steam.
- 11       5.        The system of claim 4 wherein the at least one catalyst receives exhaust gas  
12               from an engine or fuel cell.
- 13       6.        The system of claim 2 wherein the at least one catalyst includes a heat  
14               exchanger in heat exchange relation with the catalyst to preheat the air, fuel and  
15               water/steam.
- 16       7.        The system of claim 1 including a plurality of catalyst sections, wherein each  
17               catalyst section receives additional air/fuel or water/steam.
- 18       8.        The system of claim 1 further including a fuel cell for receiving the hydrogen-  
19               rich gas, the hydrogen-rich gas having reduced CO content.
- 20       9.        The system of claim 8 wherein the plasmatron-catalyst system is in a vehicle.
- 21       10.       The system of claim 8 wherein the plasmatron-catalytic system is stationary.
- 22       11.       The system of claim 1 wherein the plasmatron is followed by a fuel injection  
23               system for a partial oxidation process, the fuel injection system followed by a catalyst  
24               for improved yields, the catalyst followed by water/steam injection and a water-shift  
25               reformer catalyst whereby hydrogen concentration is increased and CO concentration  
26               is decreased.
- 27       12.       The system of any of claims 1-11 wherein the catalyst is a water-shifting  
28               catalyst.
- 29       13.       The system of claim 12 wherein the catalyst is a partial oxidation catalyst.
- 30       14.       The system of claim 12 wherein the catalyst is a steam reforming catalyst.

- 1        15.     The system of claim 11 wherein the catalysts are a combination of partial  
2        oxidation, steam reforming or water-shift catalyst, with possible addition of  
3        water/steam between adjacent catalytic regions.
- 4        16.     The system of claim 15 wherein the steam reforming catalyst is followed by  
5        water-shifting catalyst with or without additional water/steam injection prior to the  
6        water-shifting catalyst.
- 7        17.     The system of claim 2 wherein the water/steam is obtained from oxidizing  
8        hydrogen in a fuel cell or by combustion in an engine.
- 9        18.     The system of claim 17 wherein an engine is a diesel engine.
- 10       19.     The system of claim 2 wherein the water/steam is obtained from the exhaust  
11       from a diesel engine.
- 12       20.     The system of claim 1 or claim 2 wherein the hydrogen-rich gas is delivered to  
13       a catalytic converter of an internal combustion engine wherein enthalpy of the  
14       hydrogen-rich gas preheats and/or activates the catalyst
- 15       21.     The system of claim 1 or claim 2 wherein the hydrogen-rich gas is used for  
16       reduction processes in metallurgy and chemistry.
- 17       22.     The system of claim 1 or claim 2 wherein the hydrogen-rich gas is used for  
18       hydrogenation as in food processing and fuel upgrading.
- 19       23.     The system of claim 1 or claim 2 further including a non-thermal catalytic  
20       reaction element to selectively oxidize CO to CO<sub>2</sub>.
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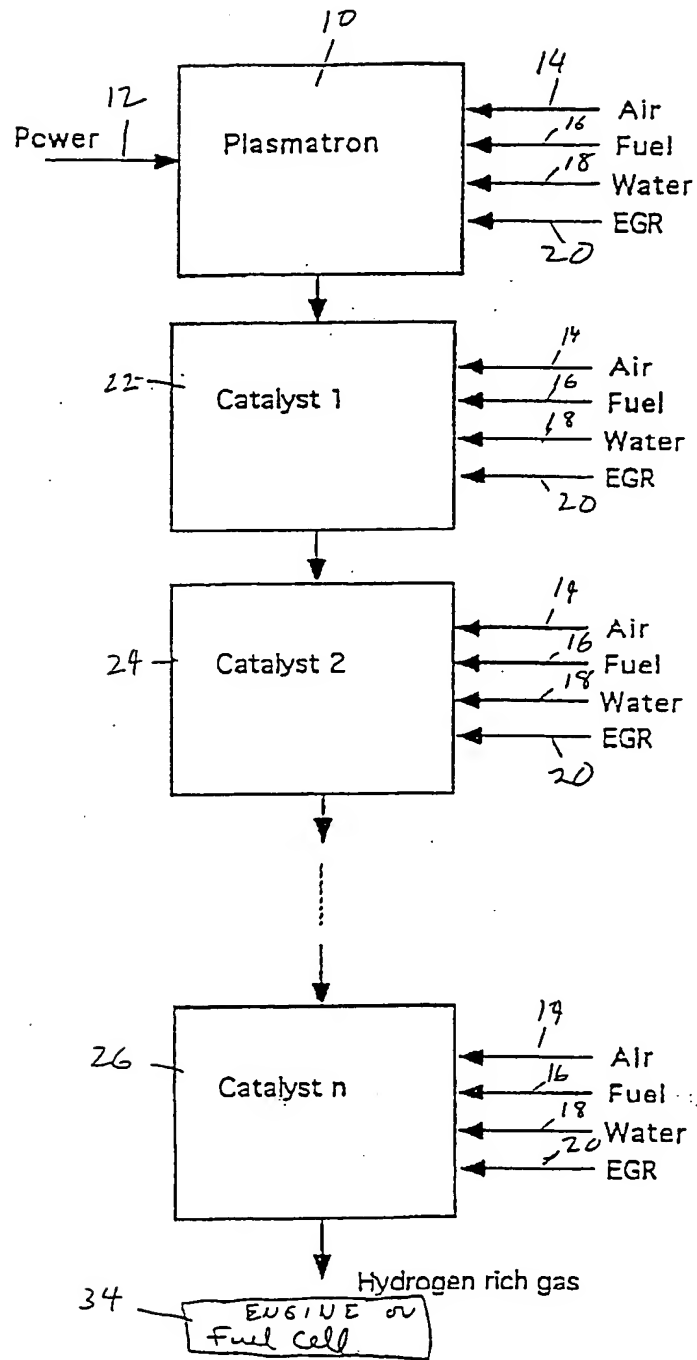


Figure 1

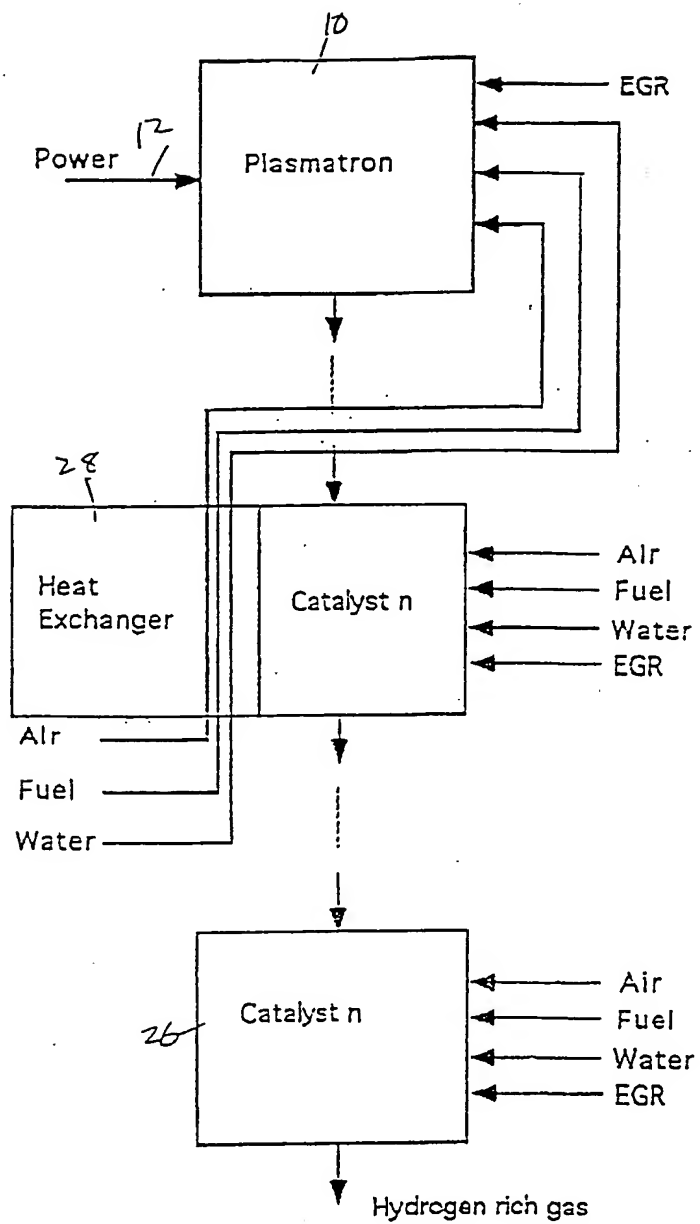


Figure 2

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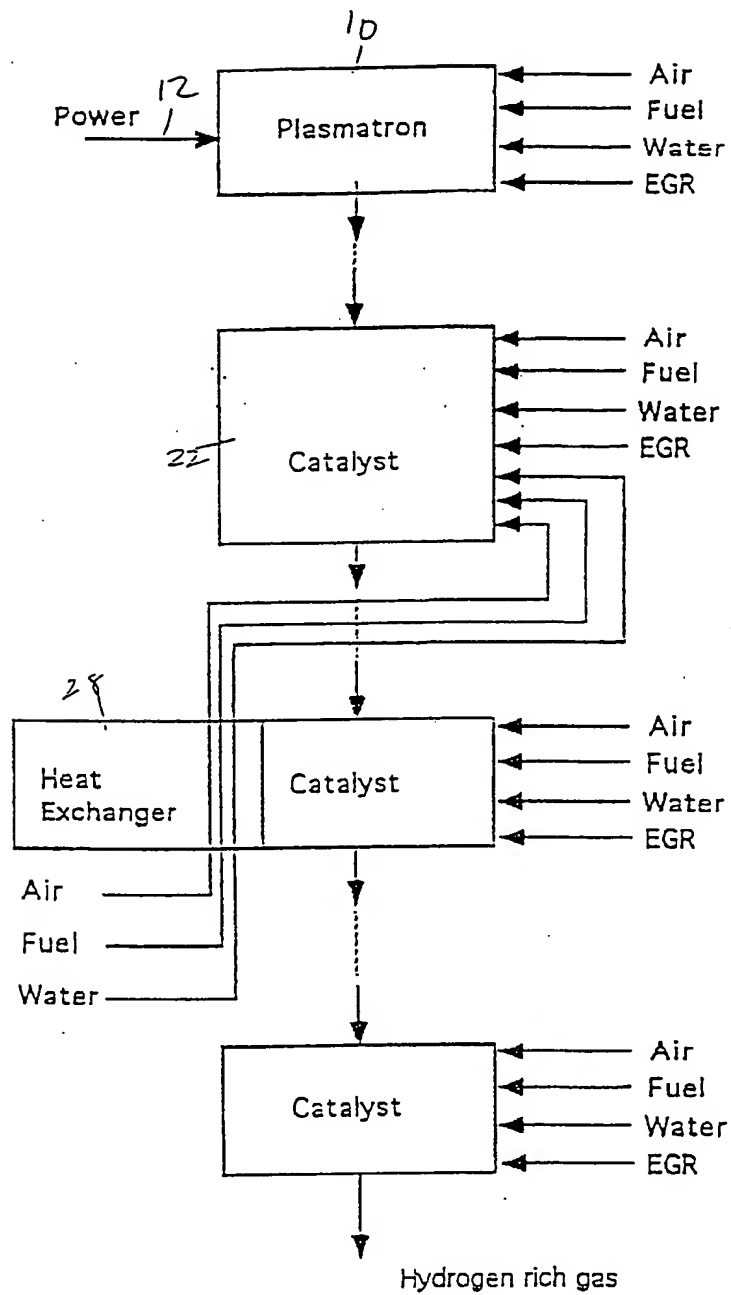


Figure 3

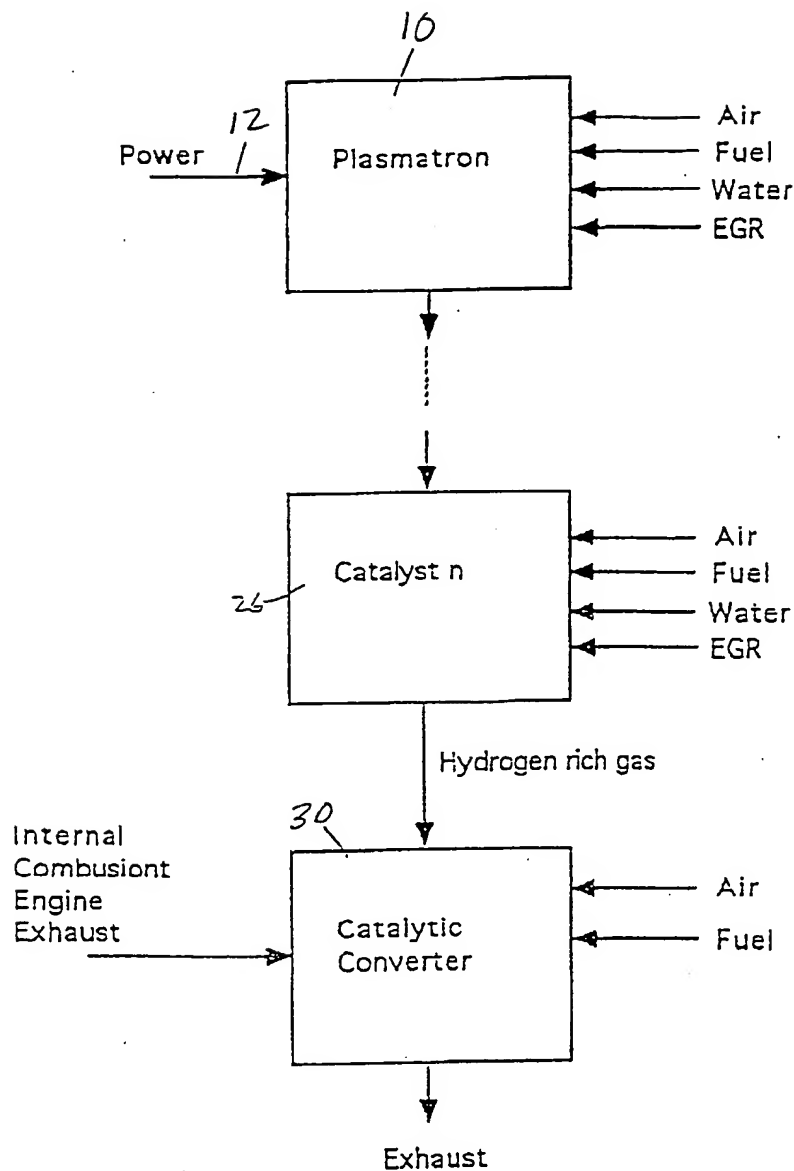


Figure 4

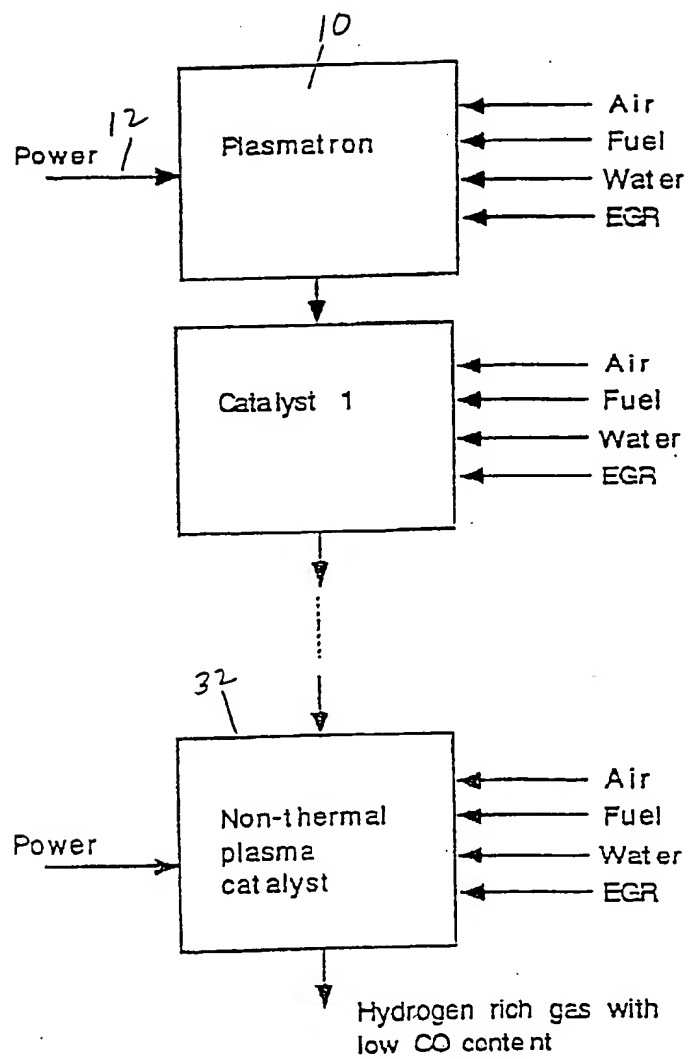


Figure 5

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 99/25179

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 F02B43/10 C01B3/34 F02B51/04

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	US 5 887 554 A (COHN DANIEL R ET AL) 30 March 1999 (1999-03-30) column 9, line 50 -column 10, line 18; figure 9 ---	1,6,9, 10,20
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

28 January 2000

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03/02/2000

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## INTERNATIONAL SEARCH REPORT

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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